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# The modified PPP (Pariser-Parr-Pople) method

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The PPP method is modified by replacing the net atomic population by gross atomic population in the matrix elements It has been shown that this simple modification greatly improves the method by inclusion of many of the one, two and three centre electron repulsion integrals

The PPP method rests upon the assumptions that atomic orbitals overlap nowhere in the space (Pariser and Parr 1953a, 1953b) Pople 1953), *i e*, if $\phi_\mu$ and $\phi_\nu$ are the two atomic orbitals in the space, then

$$d\tau = 0, \tag{1}$$

Therefore in the simplification of the Roothaan equation (Roothaan 1951) for the matrix elements

$$F_{\mu\nu} = H^c_{\mu\nu} + \sum \sum P_{\lambda\sigma}[(\mu\nu, \lambda\sigma) - \tfrac{1}{2}(\mu\lambda, \nu\sigma)] \tag{2}$$

all electron repulsion integrals $(\mu\nu, \lambda\sigma)$ defined as

$$(\mu\nu, \lambda\sigma) = \iint \phi_\mu(1)\phi_\nu(1)\frac{e^2}{r_{12}}\phi_\lambda(2)\phi_\sigma(2)d\tau_1 d\tau_2. \quad \ldots (3)$$

are neglected except $\mu = \nu$ and $\lambda = \sigma$, so that one gets

$$F_{\mu\mu} = H^c{}_{\mu\mu} + \tfrac{1}{2}P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\lambda\neq\mu} P_{\lambda\lambda}\gamma_{\mu\lambda}, \quad (4)$$

$$F_{\mu\nu} = H^c{}_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} \quad (5)$$

In eqs. (2), (4) and (5) $H^c$ is the core Hamiltonian operator defined as

$$H^c = T + \sum_q V_q \quad (6)$$

where $T$ is the kinetic energy operator and $V_q$ represents the potential due to the neutral atom $q$. $\gamma_{\mu\mu}$ stands for $(\mu\mu, \nu\nu)$

In eq. (4) $P_{\mu\kappa}$ represents the net atomic population at atom $\mu$. Now this net atomic population can be very conveniently replaced by the gross atomic population first considered by Mulliken (1955*a*, 1962, 1955b) and defined as

(7)

whence eq (4) may be modified as

$$F_{\mu\mu} = H^c{}_{\mu\mu} + \tfrac{1}{2}\gamma_{\mu\mu}\sum_\sigma P_{\mu\sigma}S_{\mu\sigma} + \sum_{\lambda\neq\mu}\sum_\sigma P_{\lambda\sigma}S_{\lambda\sigma}\gamma_{\mu\lambda} \quad (8)$$

Here the quantity $P_{\mu\sigma}S_{\mu\sigma}$ may be considered as the electronic population of the atomic overlap distribution $\phi_\mu\phi_\sigma$ and the diagonal terms such as $P_{\mu\mu}S_{\mu\mu}$ may be associated with net atomic population at atom $\mu$

Now our purpose is to show how this simple replacement improves the original *PPP* method. Consider the Roothaan equation given by eq (2). The complete expansion of this equation gives

$$F_{\mu\mu} = H^c{}_{\mu\mu} + \tfrac{1}{2}P_{\mu\mu}(\mu\mu, \mu\mu) + \tfrac{1}{2}\sum_{\sigma\neq\mu} P_{\mu\sigma}(\mu\mu, \mu\sigma) + \sum_{\lambda\neq\mu} P_{\lambda\lambda}(\mu\mu, \lambda\lambda) + \sum_{\lambda\neq\mu}\sum_{\sigma\neq\mu} P_{\lambda\sigma}[(\mu\mu, \lambda\sigma) - \tfrac{1}{2}(\mu\lambda, \mu\sigma)] \quad \ldots (9)$$

Here few terms can be merged into the others and some such as $\frac{1}{2}(\mu\lambda, \mu\sigma)$ which are very small in magnitude can be neglected, so that eq. (9) canbe re-written as

$$F_{\mu\mu} = H^c{}_{\mu\mu} + \tfrac{1}{2}\sum_\sigma P_{\mu\sigma}(\mu\mu, \mu\sigma) + \sum_{\lambda\neq\mu}\sum_{\sigma\neq\mu} P_{\lambda\sigma}(\mu\mu, \lambda\sigma). \quad (10)$$

For further simplification of this equation Mulliken's approximation (Mulliken 1949a, 1949b) for the evaluation of three and four centre electron repulsion integrals can be used. According to him

$$(\mu\nu, \lambda\sigma) = \tfrac{1}{2}S_{\mu\nu}S_{\lambda\sigma}[\gamma_{\mu\lambda} + \gamma_{\mu\sigma} + \gamma_{\nu\lambda} + \gamma_{\nu\sigma}] \quad \ldots (11)$$

Therefore on using the formula (11), we can write equation (10) as

$$F_{\mu\mu} = H^c_{\mu\mu} + 1/4 \sum_{\sigma} P_{\mu\sigma} S_{\mu\sigma} (\gamma_{\mu\mu} + \gamma_{\mu\sigma}) + \tfrac{1}{2} \sum_{\lambda \neq \mu} \sum_{\sigma \neq \mu} P_{\lambda\sigma} S_{\lambda\sigma} (\gamma_{\mu\lambda} + \gamma_{\mu\sigma}). \quad \ldots (12)$$

Here the last summation terms is a sum of two summations

$$\sum_{\lambda \neq \mu} \sum_{\sigma \neq \mu} P_{\lambda\sigma} S_{\lambda\sigma} \gamma_{\mu\lambda} \quad \text{and} \quad \sum_{\lambda \neq \mu} \sum_{\sigma \neq \mu} P_{\lambda\sigma} S_{\lambda\sigma} \gamma_{\mu\sigma}$$

which are equivalent to each other, hence eq. (12) can be re-written as

$$F_{\mu\mu} = H^c_{\mu\mu} + 1/4 \sum_{\sigma} P_{\mu\sigma} S_{\mu\sigma} (\gamma_{\mu\mu} + \gamma_{\mu\sigma}) + \sum_{\lambda \neq \mu} \sum_{\sigma \neq \mu} P_{\lambda\sigma} S_{\lambda\sigma} \gamma_{\mu\lambda} \quad \ldots (13)$$

Lastly one more approximation can be made. We can replace $\gamma_{\mu\mu}$ and $\gamma_{\mu\sigma}$ by their average value $\bar{\gamma}$, so that eq. (13) may become

$$F_{\mu\mu} = H^c_{\mu\mu} + \tfrac{1}{2} \bar{\gamma} \sum_{\sigma} P_{\mu\sigma} S_{\mu\sigma} + \sum_{\lambda \neq \mu} \sum_{\sigma \neq \mu} P_{\lambda\sigma} S_{\sigma} \gamma \quad (14)$$

It may be pointed out that if $\gamma_{\mu\mu}$ and $\bar{\gamma}$ are left empirical parameters, then there is a close similarity between equations (14) and (8). In deriving equation (14) we have retained most of the one, two and three centre electron repulsion integrals It can be concluded therefore that the replacement of the net atomic population by gross atomic population improves the *PPP* method by including most of the one to three centre integrals in the diagonal matrix elements.

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